

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



37

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |  |   |  |
|--|--|---|--|
| (51) International Patent Classification <sup>7</sup> :<br><b>B32B 17/10, C03C 27/12, B60J 1/00,<br/>E06B 3/66</b>   |  | A1  | (11) International Publication Number: <b>WO 00/48832</b>      |
|  |  |   | (43) International Publication Date: 24 August 2000 (24.08.00) |
| (21) International Application Number: PCT/US00/04074  |  | (81) Designated States: BR, CA, JP, KR, MX, PL, European patent<br>(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT,<br>LU, MC, NL, PT, SE). |  |
| (22) International Filing Date: 17 February 2000 (17.02.00)  |  |   |  |
| (30) Priority Data:<br>60/120,884 20 February 1999 (20.02.99) US<br>09/328,959 9 June 1999 (09.06.99) US   |  | Published<br><i>With international search report.</i>   |  |
| (71) Applicants: SAINT-GOBAIN PERFORMANCE PLASTICS CORPORATION [US/US]; 150 Dey Road, Wayne, NJ 07470 (US). SAINT-GOBAIN VITRAGE [FR/FR]; "Les Miroirs", 18, avenue d'Alsace, F-92400 Courbevoie (FR).   |  |   |  |
| (72) Inventors: FRIEDMAN, Michael; 10 Wills Avenue, Wayne, NJ 07470 (US). MCDONNELL-LEE, Deirdre, C.; Apartment 3S, 4406 Martha Avenue, Yonkers, NY 10704 (US). REHFELD, Marc; 6, avenue du Général de Gaulle, F-95460 Ezanville (FR). BRAVET, Jean-Louis; 5, avenue du Moulin, F-60150 Thourotte (FR). BOURE, Jean-Philippe; 2, rue de professeur René Leriche, F-92110 Clichy (FR). OFFERMANN, Volkmar; Carl-Hilt-Strasse 26, D-52134 Herzogenrath (DE).   |  |   |  |
| (74) Agents: PORTER, Mary, E. et al.; Saint-Gobain Corporation, 1 New Bond Street, Box Number 15138, Worcester, MA 01615-0138 (US).  |  |   |  |
| (54) Title: TRANSPARENT ACOUSTICAL AND MECHANICAL BARRIER  |  |   |  |
| (57) Abstract  |  |   |  |
| <p>An optically transparent glazing measures about 3 to 5 mm in total thickness, and has an interlayer film, the interlayer film comprises at least two polymeric film layers: a core film layer having a modulus of at least 25,000 psi (173 MPa) and a surface film layer having a maximum modulus of 15,000 (104 MPa) at 50 to 10,000 Hz and 20 °C; and the glazing is characterized by an acoustical barrier insulating capacity at least equivalent to that of a 3.85 mm thick monolithic pane of glass. The glazing also has an Articulation Index value of less than 64.2 % at 50 to 10,000 Hz, a sharpness value of less than 150 at 50 to 10,000 Hz, a penetration resistance of at least 9 meters in test method ECE R43, A6 4.2, and a maximum haze of 4 %. The interlayer film has a bending stiffness of at least 0.01 Pa*m<sup>3</sup>. The surface film layer has a maximum tan delta of 0.6 at 50 to 10,000 Hz and 20 °C. The interlayer film preferably comprises one core film layer of between 1.0 and 1.7 mm in thickness within two surface film layers, each between 0.2 and 0.6 mm in thickness. The glazing preferably comprises a glass/interlayer film glass sandwich having a glass/film thickness ratio from 4.2/0.8 to 1.0/2.8.</p> |  |   |  |

Transparent Acoustical and Mechanical Barrier

This application claims the benefit of U.S. provisional application number 60/120,884, filed February 20, 1999. The invention relates to polymeric interlayer films useful in light-weight, impact resistant, transparent glass or plastic laminates. The glass laminates are effective as transparent acoustical and mechanical barriers when used as side lights, back lights and sky roofs in automobiles and other vehicles, as well as in architectural applications.

Many polymeric interlayer materials and lamination designs have been described for use in automotive and architectural glazing applications. Industry, government and customer specifications for safety, impact resistance, ultraviolet and infrared light blockage, moisture resistance, haze or optical clarity, sound transmission, weight and thermal transmission direct the selection of materials and designs for particular glazing products. In general, manufacturers require lighter weight, thinner glazing products for automotive assembly than for architectural uses.

Impact resistance and controlled patterns of glass shattering are specified safety parameters for automotive glazing products. To meet these parameters, automotive glazing products are generally constructed of a multi-layer laminate of a glass sandwich containing a polymeric interlayer film. Many automobile-makers require security or anti-theft properties in glazing products in addition to mandatory safety properties. For deterring unauthorized entry into a vehicle, to lessen the likelihood of a person being thrown from a vehicle during an accident and for acceptable security functionality, the glazing products must possess high penetration resistance and high rigidity after glass breakage.

Among the polymeric interlayer materials described as useful in security and safety glass laminations are the high modulus "ionomeric resin" materials used as a film interlayer between two rigid transparent sheets in the manner described in U.S.-A-4,668,574. In general, an adhesion promoter, e.g., a silane primer, is needed to laminate the ionomeric resin to glass, and the ionomeric resin is preferably cross-linked, e.g., with a diamine, to increase its effective use

sealed laminate, as in windshield constructions, the tendency of the PVB film to absorb moisture is not a problem. For other vehicular glazings, such as side lights (windows in side doors having no perimeter gasket or seal), conventional PVB film absorbs water too readily to permit acceptable use life. More complex and costly moisture resistant PVB resin formulations, such as those described in U.S.-A-4,952,457, have been developed for unsealed glazing.

When PVB film is used as the sole interlayer film, glazing laminates do not deliver desirable security performance because they have insufficient rigidity after glass breakage due to the low stiffness of the PVB interlayer. An opening can be made too easily between the glazing and the surrounding body of the vehicle. Neither monolithic glass panes, nor PVB film interlayer laminates, provide an adequate security barrier.

Many different types of polyurethane films have been used in automotive glazings. Some polyurethane films are similar to PVB films in their mechanical properties. In WO 98/50228, certain rigid thermoplastic polyurethanes having a Young's modulus of about 2,000 MPa are suggested interlayer films for glazings characterized by a high intrusion resistance. Many have slightly better acoustical barrier attributes than PVB films, but fail to provide an adequate security barrier. Furthermore, as described in U.S.-A-5,368,917 the polyurethane films tested yielded inadequate acoustical insulating barriers for automotive glazing products.

Acoustical barrier requirements for glazing products are defined in U.S.-A-5,368,917 for the range of frequencies detectable by the human ear, i.e., about 400-15,000 Hertz, with the most critical range falling between 500 to 10,000 Hertz. The standards in this patent are based on the performance of either a 10 mm or a 5 mm thick monolithic glass pane.

Thus, an acoustical barrier glazing has been traditionally understood to be a barrier providing a level of acoustic comfort within the vehicle or building comparable to the level of acoustic comfort provided by a conventional monolithic glass barrier for a given intensity and quality of environmental noise.

Glass (e.g., soda-lime-silicate mineral glass) provides a good acoustical barrier and, over a critical frequency range of about 800 to 10,000 Hz, is most effective at a total glazing thickness of at least about 10 mm. Effective glass glazing

comprising, respectively, 70-81.8 mole% degree of butyralization and 60-68 mole% degree of butyralization. A plasticizer is used in both films.

A silicone/acrylate resin vibration damping film is disclosed in U.S.-A-5,624,763. This silicone/acrylate resin ("ISD resin") is suggested for use in applications requiring damping over a wide temperature range (-50 to 200°C) and is described as having damping performance that is substantially independent of temperature in this range. The use of this ISD resin, in combination with two layers of polyester resin and two layers of PVB resin, as an acoustic damping interlayer film for glass laminates is disclosed in DE-1 97 05 586 C1.

None of these "acoustic resin" films would be effective as a security barrier in glazing laminates, and many exhibit undesirable optical properties.

Furthermore, in newer models of automobiles, a glass thickness of 3 to 5 mm has been specified for side lights so as to minimize the contribution of the glazing to the overall weight of the automobile. At the same time automobile manufacturers seek to reduce the weight of the glazing, they also want to maintain the acoustical barrier and security barrier properties of the glazing. The automobile manufacturers increasingly want to respond to consumer demands for a better quality sound environment in the automobile, and to go beyond existing products generally designed to control only the volume of background noise, without regard to whether the type of noise is offensive to humans. Evidence of this trend can be seen in U.S.-A-5,805,457, the contents of which are hereby incorporated by reference, wherein roughness, dissonance, sharpness and boom measurements are made over frequencies based upon the musical scale interval to predict aesthetic qualities of noise audible to humans in the interior of a vehicle. In particular, a sharpness value is identified as being significant to human perceptions of noise quality. Lower sharpness values are less offensive to the human ear than high values. Other aesthetic factors include Articulation Index values and loudness values over the relevant frequency range. Articulation Index is described in detail in U.S.-A-5,729,658, which is hereby incorporated by reference. Articulation Index is a measure of the intelligibility of speech and other sounds in the acoustic range and it may be evaluated in a relative manner over multiple listening conditions. For a passenger in a vehicle, exterior speech or noise that is intelligible is more

transmission. The resultant acoustical barrier properties are unexpected, given the material properties and thickness of the materials employed in the glazing.

When used in glass laminates, this multi-layer film has optical clarity, along with good adhesion to glass, the mechanical properties needed to meet safety and security standards and moisture resistance required for automotive glazing products, including automotive side lights. Optically transparent glazing containing the acoustical barrier, security barrier multi-layer film made according to our invention also may be used in less demanding glazing applications, such as architectural glazing.

The invention is an optically transparent glazing, measuring about 3 mm to 5 mm in total thickness, and having an interlayer film, the interlayer film comprising at least two polymeric film layers: a core film layer having a modulus of at least 25,000 psi (173 MPa), and a surface film layer having a maximum modulus of 15,000 (104 MPa) at 50 to 10,000 Hz and 20 °C; and the glazing having an acoustical barrier insulating capacity at least equivalent to that of a 3.85 mm thick monolithic pane of glass, an Articulation Index value of at least 64.2% at 50 to 10,000 Hz, a sharpness value of less than 150 at 50 to 10,000 Hz, a penetration resistance of at least 9 meters in test method ECE R43 A6 4.2, and a maximum haze of 4%. The interlayer film has a bending stiffness of at least 0.01 Pa \*m<sup>3</sup>. The interlayer film comprises a surface film layer having a maximum tan delta value of 0.6 at 50 to 10,000 Hz and 20°C. The interlayer film preferably comprises one core film layer of between 1.0 and 1.7 mm in thickness within two surface film layers, each between 0.2 and 0.6 mm in thickness. The glazing preferably comprises a glass/interlayer film glass sandwich having a glass/film thickness ratio from 4.2/0.8 to 1. 0/2.8.

Figure 1 is a graph illustrating the acoustic properties of a model glass/film glazing at different thickness of film and glass layers and at different Young's Modulus values. The model is described in more detail in Example 4.

Figure 2 is a graph illustrating the relationship between the equivalent Young Modulus for a given mass of the multi-layer film and the Sound Transmission Loss (ratio of incident sound energy to transmitted sound energy in dB/Hz) for the test glazing laminates. Differences in Sound Transmission Loss occur only in the coincidence frequency range corresponding to dips in the curves. Curve areas

layer, provided at a thickness of at least 0.8 mm using materials having a modulus of at least 25,000 psi (173 MPa) and present as an interlayer between two 1.1 mm glass sheets, is characterized by sufficient impact resistance to meet automotive security standards. Suitable "security" laminates comprising this core layer have a penetration resistance of at least 9 meters in the ball drop test method ECE R43 A6 4.2. Suitable interlayer films have a bending stiffness of at least 0.01 Pa \* m<sup>3</sup>. When installed as automotive side-lights, the security glazing resists repeated blows (e.g., 5-10) with a heavy object (e.g., a 1-2 kg weight) such that the interior of the automobile is secure against typical accidental or criminal assaults. A security glazing comprising a core layer film at a thickness of at least 0.8 mm (e.g., for cross-linked ionomeric resin) wherein the core layer material has a dynamic modulus of at least 25,000 psi (173 MPa) in the frequency range from 50-10,000 Hz, has sufficient mechanical strength to resist such assaults.

In addition to the DuPont ionomeric resins described above, suitable materials for use in the core layer include resin films of Iotek ionomeric resin (copolymers of carboxylic acids obtained from Exxon Corporation), IMAC ionomeric resin (obtained from Chevron Corporation), and polycarbonate, PET, polybutylene terephthalate (PBT), PVC resins, and impact-resistant, rigid thermoplastic polyurethane (e.g., IsoplastTm rigid polyurethane materials (with sufficient minimum modulus) available from Dow Chemical Company) and combinations thereof. The resins may be crosslinked and/or mixed with additives as desired.

The "surface layer" (or "surface film layer" or "adhesive or skin layer" or "soft film layer") may comprise EVA, ethyl acrylic acetate (EAA), ethyl methacrylate (EMAC), metallocene-catalyzed polyethylene (m-PE), plasticized PVC, plasticized PVB, ISD resins (US-A-5,624,763 and U.S.-A-5,464,659), polyurethane, acoustic modified PVC (e.g., the acoustic modified PVC of US-A-4,382,996, available from Sekisui KKKK, Osaka, Japan, and further described in interlayer films of US-A-5,773,102), and acoustic modified PVB (e.g., JP-A05138840), and combinations thereof.

Materials adherent to mineral glass without the application of a primer, such as EVA, are preferred adhesive layers herein because they reduce the cost and complexity of the glazing. Transparent, non-yellowing, temperature and light stable grades of these resins are preferred.

Published, and/or measured, modulus values for examples of high clarity, polymeric materials suitable for making the core layer are shown in Table 1.

Table I Modulus of Core Layer Materials-ASTM Method D-638

Core Layer >25,000 psi (> 173 MPa)

|    | <u>Polymer</u>  | <u>Tg (°C)</u> | <u>Modulus psi (MPa) a</u>       |
|----|---|----------------|----------------------------------|
| 5  | Suryln 8140 ionomer uncross-linked<br>(E. I. Dupont NeMours, Wilmington, DE)  | 40-50          | 55-60,000 (379 - 414)            |
|    | Surlyn 8140 ionomer, cross-linked<br>(E. I. Dupont NeMours, Wilmington, DE)   | 40-50          | 70-80,000 (483 - 552)            |
| 10 | Surlyn 8920 ionomer, uncross-linked<br>(E. I. Dupont NeMours, Wilmington, DE) | 40-50          | 34-37,000 (235 - 255)            |
|    | Iotek 8030 ionomer<br>(Exxon Chemical Co, Baytown, TX)                        | 40-50          | 34-37,000 (235 - 255)            |
|    | Surlyn 8920 ionomer, cross-linked<br>(E.I. Dupont NeMours, Wilmington, DE)    | 40-50          | 37-39,000 (255 - 304)            |
| 15 | Polycarbonate<br>(G.E. Company, Pittsfield, MA)                               | 150 b          | 345,000 (2,379)                  |
|    | PET<br>(Ticona, Summit, NJ)   | 80 c           | 400 - 600,000 (2,759 - 4,138)    |
| 20 | PBT(Crastin PBT)<br>(E.I. Dupont NeMours, Wilmington, DE)                     | 50-55 d        | 390-2,000,000 (2,690 - 13,793) d |
|    | Rigid PVC<br>(Geon Company, Avon Lake, OH)                                    | 75-100 d       | 336,700 (2,322) d                |

a. Modulus values were determined by ASTM D638 method.

25 b. This Tg value is taken from Encyclopedia of Polymer Science and Engineering, (2<sup>nd</sup> Edition) 1986, Vol. 11, page 657.

c. This Tg value is taken from Polymeric Materials Encyclopedia (1st Edition) 1996 page 6078). All Tg values other than those of b. and c. were measured on a DSC 200 Differential Scanning Calorimeter (Seiko Instruments Corp., Japan).

30 d. Data obtained from suppliers of resin materials.

Other core layer materials having a modulus less than 25,000 psi (173 MPa) may be used herein, provided that the resultant interlayer film made with the

Acoustic modified PVB e

140

(Sekisui KKKK, Osaka, Japan)

- a. Modulus values were determined by ASTM D638 method.
- b. Values were obtained from suppliers' technical data sheets for these product samples.
- 5 c. All other Tg values were measured on a DSC 200 Differential Scanning Calorimeter (Seiko Instruments Corp., Japan).
- d. See US-A-5,624,763 for a description of the acrylic/silicone resin materials used in the ISD resins.
- e. See JP-A-05138840 for a description of the acoustic modified PVB resin.

10

Other surface layer materials having a modulus in excess of 15,000 psi (104 MPa) may be used herein if the material has a suitable tan delta value. In the past, materials having a tan delta of at least 0.5 were believed essential to creating an acoustic barrier. Rather unexpectedly, preferred surface film materials for the laminated glazing of the invention have a tan delta value in the range from a minimum of 0.1 to a maximum of 0.6, provided the materials control the aesthetic quality of the transmitted sound (i.e., sharpness value, loudness and Articulation Index).

15

As used herein "tan delta" is a temperature and frequency dependent ratio of the loss modulus to the storage modulus (i.e.,  $G''/G'$ ). In other words, the tan delta is the ratio of the portion of mechanical energy dissipated to the portion of mechanical energy stored (springiness) when a viscoelastic material undergoes cyclic deformation. Optimum damping of sound occurs at the maximum tan delta and more damping occurs when viscoelastic material is constrained in a sandwich than when it is extended or compressed.

20

25

The relative thickness ratios of the core layer, the surface layer and the glass panes should be selected so as to optimize the combination of acoustical barrier properties and security barrier properties of the multi-layer film.

The relatively high density of glass makes glass a good acoustical barrier, but weight limitations in vehicles dictate a preferred ratio wherein the glass thickness is minimized. For polymeric materials having a modulus of at least 25,000 psi (173 MPa), a core film thickness of at least 0.8 mm for a cross-linked ionomeric material and at least 1.0 mm for non-cross-linked ionomeric material, in combination

30



Cyanamid (Basel, Switzerland), and polymerizable benzotriazole (NORBLOCK®) absorber, supplied by Noramco Corporation (USA). Absorbers should be used in concentrations in the range from about 0.1% to about 1.5%, preferable in the range from about 0.25% to about 1.5%, and most preferable in the range from about 1.0% to about 1.5%.

Nucleation agent may be added to improve optical properties and clarity; to reduce the haze of the film, and to stabilize the morphological structure of the material. Incorporation of a nucleation agent helps to reduce the dimensions of crystalline units and provides stability after reheating of the film during lamination or after exposure to sun or other sources of heat.

Very small particles of minerals can also be used as nucleation agents. Pigments, dyes, and/or color concentrates may be added when special color effects are needed in the safety glass or plastic laminate for architectural, decorative and other applications. They are used in such concentrations as are determined by coloration technology.

Other additives can also be incorporated to achieve special properties of the interlayer and resultant interlayer film product such as, for example, to achieve reduced IR-light transmittance; to increase reflection, and to decrease the blocking and to improve the slipping of film. A liquid elastomer, such as Isoprene-Butadiene-Isoprene resin available from Mobil Chemical Co., may be added to the ionomeric resin for the purpose of impact modification and as a processing aid.

An interlayer film product according to the present invention may be smooth surfaced or it may also have embossed patterns on its surface which assist the evacuation of air between the glass plates (sheets) and the interlayer during lamination. The film may have embossed patterns on one or both sides made with an embossing roll. Patterns also may be created using an extrusion die with a specific design profile.

Cross-linking of the polymer according to the present invention can be achieved by different techniques. The peroxide technology using organic peroxides (for example dicumyl peroxide) incorporated into the formulation is very efficient. It increases the use temperature up to at least 20\*-70°C. Preferred cross-linking materials suitable for use herein include di-cumyl peroxide with an initiator, dibutyltin

In those formulations containing additive premixtures, these additives pellets were combined (at 2 wt%) with ionomeric resin, and, optionally, another additive premixture. The second additive premixture contained the components identified in Table 3. These components were premixed in a dry high speed mixer for 20 minutes and then extruded using a Davis Standard 35 Mark V single screw extruder (9 mm screw diameter) with a 140 mm wide coat hanger die. This single screw extruder had the following barrel temperatures: feeding zone #1 - 125-135 °C, feeding zone #2: 129-139 °C, feeding zone #3: 145-155 °C, feeding zone #4- 148-158 °C, and die plate: 153-162 °C. The speed of the screw was between 10 and 17 rpm.

Each film was extruded and cooled using a three roll casting roll stock and was wound onto 7.6 cm cores. Fifteen samples were cut for testing from each film produced. At each of five sampling locations which were 10 linear feet (4.05 m) apart, samples were obtained at three points across the film web (from each of the edges and from the middle).

Ionomeric resins used in these films included the 8140 grade and the 8920 grade of Surlyn® resin obtained from DuPont Nemours, Wilmington, DE. The EVA resin used in these films was obtained from Specialized Technologies Resources, Inc., Enfield, CT under the Photocap™ 15295P designation.

#### Film testing procedures

Film samples produced according to the above description were tested for the parameters listed below in Tables 3-8, as described in the following Tables and Examples. All films listed in Table 3 were extruded at 1.4 mm (56 mil gauge) thickness. Film samples F7, F8, F10, F11 and F13 were co-laminated with EVA film in a 0.2/1.4/0.2 mm thick sandwich configuration. All EVA resin, except the resin used in one of the F11 film samples (used to make laminate sample L19, Table 4), was Photocap™ 15295P EVA resin from STR. The L19 sample was made using a film of SG12514U38 grade EVA resin obtained from Bridgestone Corporation, Yokohama, Japan.

ethylene methacrylic acid, estimated to contain about 15 wt% acid, obtained from DuPont Nemours, Wilmington, DE.

8140 Surlyn Grade 8140 resin is a partially sodium neutralized copolymer of ethylene methacrylic acid, estimated to contain more than 17 wt% acid, obtained from DuPont Nemours, Wilmington, DE.

Adequate cross-linking to prevent flow of the film at elevated automotive side light use temperatures was achieved in resin samples having a gel content of at least 50 % (by Gel Content analysis - ASTM D2765-95; D3351 - Test Method for Gel Count of Plastic Film).

The UV light transmission, haze and Yellow Index were measured after laminating a layer of 0.5 to 2.5 mm film between two layers of 1.1 to 3.1 thick sheets of clear, soda-lime-silicate glass as described below. The UV light transmission was measured using ANSI Standard Z26.1T2. The haze was measured using the ASTM D1003-95 Standard. Yellow Index was measured using ASTM E 313-96 Method.

For automotive glazing, 2% or less UV transmission and 2% or less haze are acceptable. For general glazing purposes, 4% or less haze and 4% or less UV transmission are acceptable. As shown below in Table 4, film samples F7 and F9 made with UV additives, and co-laminated film F7 sandwiched between EVA films and used as an interlayer film, made glass laminates suitable for automotive glazing. In general, the 8140 resin exhibited less haze and yellow index percentages in glass laminates than the 8920 resin, but the 8920 resin was acceptable for use herein with appropriate additives and handling. The 8920 resin required crosslinking treatment (F11) to yield acceptable optical properties. UV additives and liquid elastomer can be added to improve film processing and to give optical properties suitable for automotive use (see F12 and F13 film samples).

In treatment levels of >2 wt.% BAC crosslinking agent in the 8140 resin, the BAC caused the Yellow Index of the ionomer to exceed 2%, a percentage which is unacceptable for automotive applications. This result was not observed for the DCPR and BPDH peroxide crosslinking agents at the levels used in these film samples. Example 2

#### Glass Laminate Preparation

Example 1 are show below in Tables 4 and 5.

Table 4 Glass Laminates from films of Table 3

|    | Laminate | Film                         | Haze (%) | Yellow Index | %UV          |
|----|----------|------------------------------|----------|--------------|--------------|
|    |          | (mm)                         |          | %            | transmission |
| 5  | L1       | F1                           | 0.3-0.5  | 0.4          | >35          |
|    | L2       | F2                           | 0.7-0.9  | 1.9          | >35          |
|    | L3       | F3                           | 0.6-0.8  | 4.0          | >35          |
|    | L4       | F4                           | 0.6-0.8  | 1.8          | >35          |
|    | L5       | F5                           | 0.4-0.6  | 0.6          | >35          |
| 10 | L6       | F6                           | 0.5-0.7  | 0.8          | >35          |
|    | L7       | F7                           | 0.5-0.7  | 1.52         | 0.04         |
|    | L8       | F8                           | 0.5-0.7  | 1.25         | >35          |
|    | L9       | F9                           | 1.0-1.2  | 1.94         | 0.02         |
|    | L10      | F10                          | 1.0-1.2  | 1.83         | 14           |
| 15 | L11      | F11                          | 0.6-0.8  | 1.27         | 13.7         |
|    | L12      | F12                          | 3.3      | 8-9          | >35          |
|    | L13      | F13                          | 1.2      | 2.96         | 12.9         |
|    | L14      | co-laminate<br>EVA/F7/EVA    | 1-1.2    | 1.2          | 0.01         |
| 20 | L15      | co-laminate<br>EVA/F8/EVA    | 1.9-2.2  | 3.1          | 10.2         |
|    | L16      | co-laminate<br>EVA/F 10/EVA  | 4.2-4.4  | 4.5          | 3.0          |
|    | L17      | co-laminate<br>EVA/F 11 /EVA | 1.8-2.0  | 1.73         | 5.6          |
| 25 | L18      | co-laminate<br>EVA/F1 3/EVA  | 2.5-2.7  | 2.1          | 4.2          |
|    | L19      | co-laminate<br>EVA/F 11 /EVA | 1.5-1.7  | 3.0          | 0.16         |

Adequate adhesion of the ionomer resin film to the glass sheets was achieved in ionomeric resin samples L20a to L24 and control 2 only by utilizing a

Table 5

| 5  | Laminate/<br>Test | Film Resin                       | Primer | Pummel             | Thickness       | Impact   |
|----|-------------------|----------------------------------|--------|--------------------|-----------------|----------|
|    | Film              |                                  |        | Value <sup>a</sup> | Glass/          | limiting |
|    | drop              |                                  |        |                    | Interlayer/     | height   |
|    | Sample<br>(m)     |                                  |        |                    | Glass (mm)      | w/ 226g  |
|    | ball <sup>b</sup> |                                  |        |                    |                 |          |
| 10 | LC1/FC1           | PVB film <sup>c</sup>            | No     | 4-8                | 1.6/0.76/1.6    | 6        |
|    | L20a/F1           | 8140 ionomeric resin             | Yes    | 6-8                | 1.1/1/1.1       | 5        |
|    | Extruded          |                                  |        |                    |                 |          |
|    | 1mm               |                                  |        |                    |                 |          |
|    | L20b/F1           | 8140 ionomeric resin             | Yes    | 6-8                | 1. 1/2x1 /1. 1  | 10       |
| 15 | L21 /F4           | 8140 ionomeric resin/            | Yes    | 6-8                | 1.1/1/1.1       | 10       |
|    | Extruded          | X-link + elastomer               |        |                    |                 |          |
|    | 1mm               |                                  |        |                    |                 |          |
|    | L22/F4            | 8140 ionomeric resin/            | Yes    | 6-8                | 1. 1 /2x1 /1. 1 | >1       |
|    | 3.5               |                                  |        |                    |                 |          |
| 20 |                   | X-link + elastomer               |        |                    |                 |          |
|    | LC2/FC2           | Noviflex® ionomeric              | Yes    | 6-8                | 1.1/2/1.1       |          |
|    |                   | >13.5                            |        |                    |                 |          |
|    |                   | Resin film <sup>d</sup>          |        |                    |                 |          |
|    | L23/F7            | 8140 ionomeric resin/            | Yes    | 6-8                | 1.1/1.4/1.1     | 8        |
| 25 |                   | X-link + elastomer               |        |                    |                 |          |
|    | L24/F7            | 8140 ionomeric resin/            | Yes    | 6-8                | 1. 1/2x1 /1. 1  | 8        |
|    |                   | X-link + elastomer               |        |                    |                 |          |
|    | L25/F7            | *EVA/8140 resin/EVA <sup>e</sup> | No     | 6-8                | 1.1/0.2-1-0.2   | 12       |
|    | Extruded          |                                  |        |                    | /1.1            |          |
| 30 | 1mm               |                                  |        |                    |                 |          |
|    | L26/F7            | *EVA/8140 resin/EVA <sup>e</sup> | No     | 6-8                | 1.1/0.2-1.4-0.2 | >13.5    |
|    |                   |                                  |        |                    | /1.1            |          |

a. Pummel value was determined by cooling laminated samples to -20° C for 24 hrs, removing the samples from the cooling chamber, immediately striking them with a flat-headed hammer until the glass has been shattered, and then visually evaluating the

## Example 3

The compositions listed below in Table 6 were tested for viscoelastic properties on a Dynamic Mechanical Thermal analyzer (DMTA) (Viscoanalyseur VA 815+, obtained from Metravib Company) at 5 to 400 Hz and -10 to 90°C (extrapolated to frequencies of 50 to 10,000 Hz), and the results (dynamic or storage modulus ( $G'$  at 20° C and 200 Hz),  $\tan \delta$  ( $G''/G'$ ) and TMA) are shown in Table 6. Film samples from Example 1 were prepared for testing by laminating five (1 mm thick) sheets of the film between two release sheets within two sheets of glass using the lamination and autoclave process described in Example 2, above. The DMTA testing was carried out on the single sheet of laminated film 5 mm in thickness after removing the film from the glass and release sheets.

Table 6

| Film sample <sup>b</sup>    | $G'$ (MPa) | $\tan \delta$ | TMA (°C) |
|-----------------------------|------------|---------------|----------|
| Noviflex resin film         | 167        | 0.070         | 98       |
| 15 F1 (5 mm)                | 320        | 0.049         | 103      |
| F-4 (5 mm)                  | 309        | 0.052         | 118      |
| "                           | 287        | 0.050         |          |
| "                           | 252        | 0.067         |          |
| "                           | 253        | 0.065         |          |
| 20 "                        | 254        |               |          |
| F-7 (5 mm)                  | 273        | 0.059         | 98       |
| "                           | 277        | 0.059         |          |
| EVA (peroxide               | 41         | 0.19          | 107      |
| cross-linked, STR grade)    | 47         | 0.16          |          |
| 25 ionomeric resin          | 267        | 0.054         | 105      |
| (DuPont Sentry Glass Plus®) |            |               |          |
| PVB <sup>c</sup>            | 140        | 0.30          |          |
| PVB acoustic <sup>d</sup>   | 0.7        | 0.90          |          |
| 3.85 mm glass               | 24,000     | 0.03          |          |
| 30 ISD resin <sup>a</sup>   | 0.9        | 0.7-0.9       |          |

a. The  $\tan \delta$  value was reported in US-A-5,624,763 for the ISD resin.

account the aesthetic character of the acoustic transmission, a variable that has become important to acceptance of a glazing for vehicular use.

Calculations of the aesthetic qualities (sharpness, loudness and Articulation Index %) of acoustic performance in vehicular sidelights were made using a database of known acoustical performance values for a 3.85 mm glass pane, and the G' and tan delta values of the multi-layer film of the invention and various comparative materials. Calculations assumed the film thickness recited in Tables 7 and 8, below. Calculations were done with a model developed on a Binaural Analysis System (BAS) signal processing system (obtained from Head Acoustics GmbH, Herzogenrath, Germany) and were derived from experimental data obtained for a Peugeot 605 vehicle in an anechoic wind tunnel at 140 km/h with 0° incident angle of wind over 100 to 5,000 Hz (made with the Artificial Head of Head Acoustics). Calculations simulate the replacement of one glazing for another glazing in the vehicle under these experimental conditions. The background noise was subtracted from the noise measured within the vehicle through a first glazing type; a transfer filter from one glazing to another was applied to the resultant noise spectrum; the background noise was added back in; and the internal noise spectrum attributable to the second (test) glazing was obtained.

The internal noise spectrum is expressed with the three parameters shown in Tables 7 and 8. Criteria used for these values were: loudness, ISO 532 B, option FFT/ISO 532; sharpness, option FFT/ISO 532; and Articulation Index, AI calculation method. These criteria are described in BAS 4.4 Binaural Analysis System Manual August 1997, Edited by Head Acoustics GmbH, Rev. 5; Part 2, Chapter 4, 4-28 & 4-70.

The results for the glazings of the invention shown in Table 7 assume the presence of two outer glass sheets, each 1.1 mm thick, in combination with the interlayer film. The film is a combination of ionomeric resin film (F7) within a sandwich of two EVA films, at the selected film thickness shown in Table 7.

Table 8

| Interlayer Film   | Glass | Glass | Total   | Loudness | Sharpness |       |
|---|-------|-------|---------|----------|-----------|-------|
| Material  | 1     | 2     | Glazing | (sones)  |           | Index |
| %   |       |       |         |          |           |       |
| (mm)  | (mm)  | (mm)  | (mm)    |          |           |       |
| Noviflex/ISD1 12 <sup>a</sup> /<br>Noviflex<br>(0.65/0.05/0.65) | 1.1   | 1.1   | 3.55    | <22.3    | <140      | >72.2 |
| PVB <sup>b</sup> (0.76)   | 1.6   | 1.6   | 3.96    | 23.1     | 144       | 65.7  |
| Noviflex <sup>c</sup> (2.0)                                     | 1.1   | 1.1   | 4.20    | 24.1     | 178       | 63.2  |
| No interlayer film;<br>Tempered glass -<br>One pane             | 3.85  | --    | 3.50    | 23       | 150       | 64.2  |

a. ISD-1 12 resin film was obtained from 3M corporation, Minneapolis, MN.

b. PVB resin was 3G grade resin obtained from Solutia, St. Louis, MO.

c. Noviflex resin film was obtained from Sully North America, Trumbauersville, PA.

These results demonstrate the optically transparent glazings and interlayer films of the invention possess the desired combination of acoustic barrier, mechanical barrier and optical transparency needed to qualify for the most demanding standards for vehicle and architectural applications.



8. The optically transparent glazing of claim 1, wherein the core film layer comprises an ionomeric resin and the surface film layer comprises an ethylene vinyl acetate resin.
9. The optically transparent glazing of claim 8, wherein the ionomeric resin and the ethylene vinyl acetate resin are each cross-linked.
10. The optically transparent glazing of claim 1, wherein the interlayer film further comprises at least one additive selected from the group consisting of UV modifiers, liquid elastomers, cross-linking agents and initiators, and combinations thereof.
11. The optical glazing of claim 1, wherein the glazing comprises at least two outer layers of a rigid, transparent material selected from the group consisting essentially of mineral glass, polycarbonate, polyacrylate, cyclic polyolefins and combinations thereof.
12. The optical glazing of claim 11, wherein the glazing further comprises a silane primer between the interlayer film and at least one of the outer layers of a rigid, transparent material.
13. The optically transparent glazing of claim 1, wherein the surface film layer is an adhesive film layer.
14. An optically transparent glazing comprising an interlayer film having a bending stiffness of at least  $0.01 \text{ Pa} \cdot \text{m}^3$ , the interlayer film comprising at least two polymeric film layers: a core film layer and a surface film layer having a maximum modulus of 15,000 (104 MPa) at 50 to 10,000 HZ and  $20^\circ \text{ C}$ ; and the glazing having an acoustical barrier insulating capacity at least equivalent to that of a 3.85 mm thick monolithic pane of glass, an Articulation Index value of at least 64.2% at 50 to 10,000 Hz, a sharpness value of less than 150 at 50 to 10,000 Hz, a penetration resistance of at least 9 meters in test method ECE R43 A6 4.2, and a maximum haze of 4%.
15. The optically transparent glazing of claim 14, wherein the glazing comprises at least two sheets of glass and one sheet of interlayer film in a glass/interlayer film/glass sandwich having a glass/film thickness ratio from 4.2/0.8 to 1.0/2.8.

22. The optically transparent glazing of claim 18, wherein the core film layer is a material selected from the group consisting essentially of copolymers of carboxylic acids, copolymers of acrylate esters, polycarbonate, polyethylene terephthalate, polybutyl terephthalate and polyvinylchloride, and derivatives thereof and
- 5 combinations thereof.

2/3

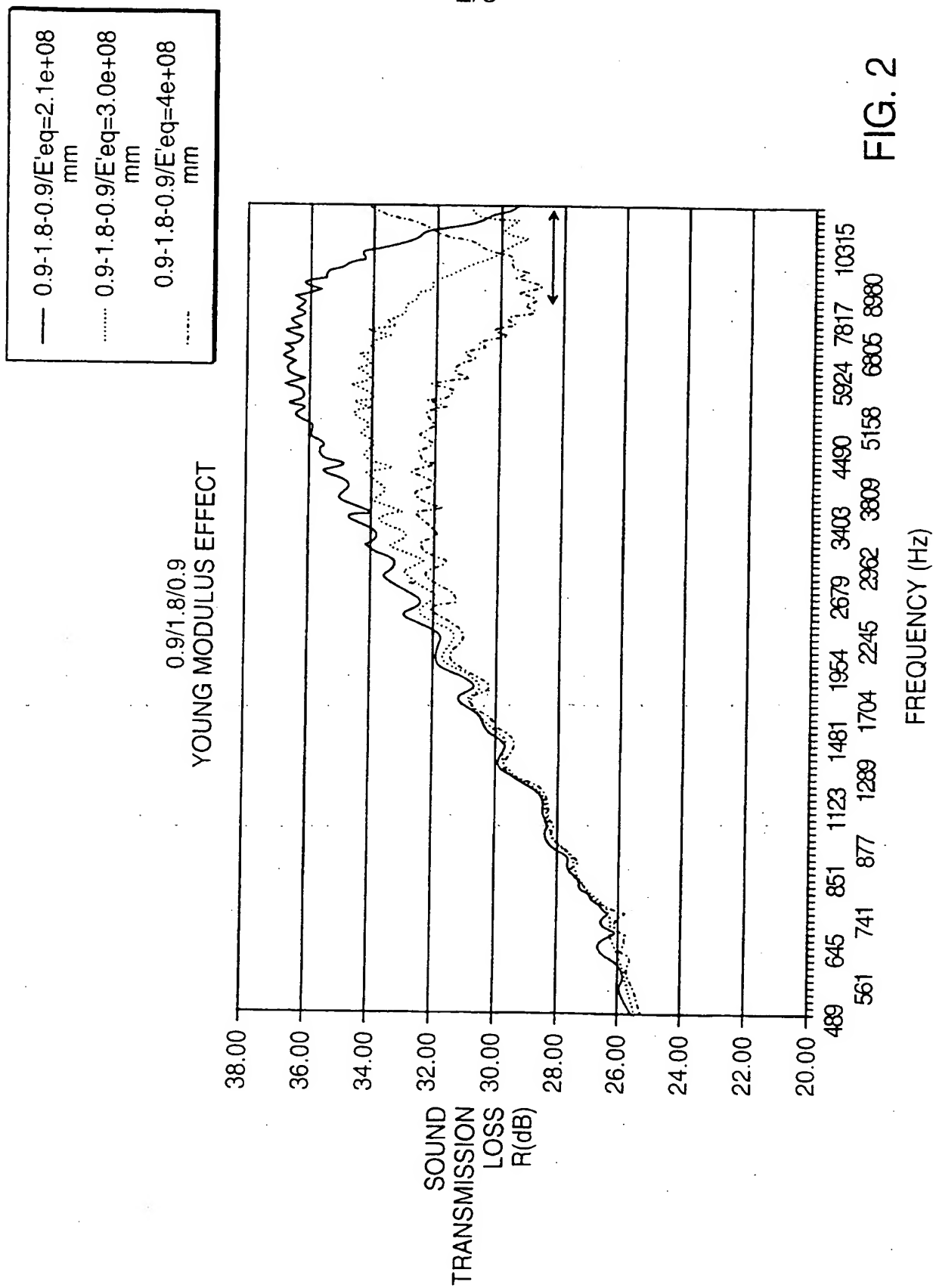


FIG. 2

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/04074

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B17/10 C03C27/12 B60J1/00 E06B3/66

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B60J E06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| X          | DE 197 05 586 C (SEKURIT SAINT GOBAIN DEUTSCH) 16 April 1998 (1998-04-16)<br>the whole document<br>---   | 1,2,5-7,<br>11,13-17  |
| X          | EP 0 517 114 A (BRIDGESTONE CORP)<br>9 December 1992 (1992-12-09)<br>examples 1-3; tables 2,3<br>claims 1,2<br>claims 3-18<br>---  | 1,2,5-7,<br>10,11,13  |
| A          | ---  | 8,9,14,<br>18,20-22   |
| X          | EP 0 852 999 A (PPG INDUSTRIES INC)<br>15 July 1998 (1998-07-15)<br>page 3, line 6 -page 4, line 37; figure 2;<br>table 1<br>page 7, line 7 - line 30<br>page 8, line 9 -page 9, line 25; table 2<br>claims 13-18<br>--- | 1,2,5-7,<br>11,13     |
|            | -/--   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

Date of the actual completion of the international search

22 May 2000

Date of mailing of the international search report

30/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Lindner, T

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/04074

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)   | Publication<br>date  |
|---|---------------------|--|--|
| DE 19705586 C                             | 16-04-1998          | EP 0844075 A<br>JP 10177390 A<br>PL 323341 A   | 27-05-1998<br>30-06-1998<br>08-06-1998   |
| EP 0517114 A                              | 09-12-1992          | JP 4362046 A<br>DE 69228776 D<br>DE 69228776 T<br>US 5632835 A   | 15-12-1992<br>06-05-1999<br>22-07-1999<br>27-05-1997   |
| EP 0852999 A                              | 15-07-1998          | US 5796055 A<br>BR 9800176 A<br>CA 2222764 A<br>FI 980043 A<br>JP 10230568 A   | 18-08-1998<br>02-03-1999<br>13-07-1998<br>14-07-1998<br>02-09-1998   |
| WO 9850228 A                              | 12-11-1998          | AU 7217998 A<br>EP 0980309 A   | 27-11-1998<br>23-02-2000   |
| US 3666614 A                              | 30-05-1972          | NONE   |  |
| EP 0844075 A                              | 27-05-1998          | DE 19705586 C<br>FR 2756225 A<br>JP 10177390 A<br>PL 323341 A  | 16-04-1998<br>29-05-1998<br>30-06-1998<br>08-06-1998   |
| WO 9826927 A                              | 25-06-1998          | BR 9713719 A<br>EP 0946359 A   | 25-01-2000<br>06-10-1999   |
| EP 0763420 A                              | 19-03-1997          | FR 2738772 A<br>BR 9603768 A<br>DE 69606939 D<br>JP 9165235 A<br>US 5773102 A  | 21-03-1997<br>02-06-1998<br>13-04-2000<br>24-06-1997<br>30-06-1998   |
| US 4784916 A                              | 15-11-1988          | FR 2549036 A<br>FR 2549037 A<br>FR 2548956 A<br>AT 31897 T<br>AU 572168 B<br>AU 3045484 A<br>BR 8403425 A<br>CA 1253425 A<br>DE 3468648 D<br>DK 337084 A, B,<br>EP 0132198 A<br>ES 534171 D<br>ES 8507435 A<br>FI 842765 A, B,<br>HU 40384 A, B<br>IL 72359 A<br>IN 161465 A<br>JP 1857912 C<br>JP 5067418 B<br>JP 60071252 A<br>KR 9205473 B<br>MX 168250 B<br>NO 842805 A, B,<br>NZ 208856 A | 18-01-1985<br>18-01-1985<br>18-01-1985<br>15-01-1988<br>05-05-1988<br>17-01-1985<br>25-06-1985<br>02-05-1989<br>18-02-1988<br>12-01-1985<br>23-01-1985<br>01-09-1985<br>16-12-1985<br>12-01-1985<br>28-12-1986<br>25-01-1994<br>12-12-1987<br>27-07-1994<br>24-09-1993<br>23-04-1985<br>04-07-1992<br>13-05-1993<br>14-01-1985<br>30-10-1987 |

This Page Blank (uspto)